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NITROGEN REMOVAL FROM WASTEWATERS

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ABSTRACT: The various forms in which nitrogen occurs in wastewater, and the equally varied methods used to remove these nitrogen compounds have been the subject of this progress report. The seven papers included provide first a brief review of some possible deleterious effects of nitrogen in the nation's wastewaters in the form of nitrites, nitrates, ammonia, ammonium ion, or dissolved nitrogen gas. Methods of removal which were studied included: (1) suspended growth biological reactors; (2) packed column biological reactors; (3) removal of ammonia nitrogen by air stripping; (4) removal of ammonia nitrogen by ion exchange; (5) removal of nitrates by ion exchange; and (6) miscellaneous other methods for removing various nitrogenous compounds. (Lowry-Texas)

(See also W72-04086 thru W72-04092)

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INTRODUCTION

Nitrogenous materials in waters have long been associated with pollution. Yet the pollutional potential of ammonia in a stream or lake is often overlooked. Conventional wastewater treatment plants are not efficient in removing nitrogen. The principles and advantages of converting organic nitrogen and ammonia to nitrates need to be understood. Removal of nitrogen can be accomplished at various stages in plant processes.

Regulatory authorities are beginning to set standards for nitrogenous materials and municipal treatment plants will be required to produce effluents low in nitrogen. The best information available is needed to provide guidelines for use of the pollution control authorities.

The Advanced Waste-Treatment Research Laboratory has conducted and sponsored several studies relating to removal of nitrogen from wastewaters. This technology is still fluid, but a great deal of useful information is available. This progress report on the status of nitrogen removal technology has been assembled by Dr. R. B. Dean with the assistance of several staff members. As more information becomes available the report will be up-dated.

F. M. Middleton
Director of Research
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NITROGEN REMOVAL FROM WASTEWATERS

Edited by Robert B. Dean
Robert A. Taft Water Research Laboratory

ABSTRACT

Ammonia and nitrates are the principal forms of nitrogen in wastewaters. Ammonia is converted to nitrates by biological oxidation and it exerts a high BOD in surface waters. Nitrates are reduced to nitrogen gas by bacteria when organic matter exceeds the oxygen supply. Both compounds are algal nutrients but ammonia is much more toxic than nitrates. The best developed method for control of nitrogen compounds is biological oxidation to nitrates followed by denitrification with the aid of methanol.

Ammonia stripping at high pH in cooling towers following lime treatment is effective but cannot be used during freezing weather and may suffer from serious scale problems. Selective ion exchange of ammonia with lime regeneration may be practical but the process is still in the pilot stage. Several other processes are being studied. A bibliography of pertinent references is attached.

Paper No. 1

NITROGEN REMOVAL FROM WASTEWATERS -- STATEMENT OF THE PROBLEM

Edwin F. Barth and Robert B. Dean

The nitrogen content of natural unpolluted waters is normally less than one milligram per liter, and during the growing season, soluble nitrogen compounds are virtually completely depleted by growing plants and algae (AWWA, 1970).* The presence of nitrogen compounds, particularly ammonia, has therefore been taken as an indication of pollution for over a century. Historically, nitrogen analyses have seniority over BOD_5 and suspended solids determinations to trace wastewater pollution and to control biological treatment. The BOD_5 tests replaced tests for various nitrogen compounds for two reasons. First, analysis was not as tedious; and secondly, the BOD_5 tests made biological processes look more efficient, since it is much easier to get 85% reduction of BOD than it is to get a comparable conversion to nitrates.

Municipal wastewaters have nitrogen contents in the 15-25 mg/l range in untreated and primary settled wastes; the nitrogen is divided between organic compounds, which are mostly insoluble, and ammonia. Biological treatment converts most of the organic nitrogen to ammonia, and under favorable conditions ammonia may be oxidized to nitrates. The conditions for nitrification of municipal effluents have been worked out by Downing and Hopwood (1964) who showed that

> "to achieve nitrification consistently, the period of aeration must exceed a minimum value which is a function of the concentration of activated sludge, the temperature, and the strength of the sewage. When conditions are favourable for nitrification, the rate of nitrification and the rate of consumption of oxygen due to this process will tend to an equilibrium level which is proportional to the concentration of activated sludge under aeration. In an aeration unit through which the liquid travels with ideal piston-flow, the concentration of ammonia in the effluent under the above conditions will be normally very small. The effect of longitudinal mixing will be to increase slightly the concentration of ammonia in the effluent."

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* All references are collected in the bibliography.

Nitrifying organisms require only NH_3 and CO_2 as major nutrients and are probably never deficient in minor nutrients in municipal wastewaters. They are, however, easily poisoned by a variety of simple substances including heavy metals and even ammonium salts at about 250 mg/l (Stojanovic, B. J., and Alexander, M., 1957). Biological nitrification of industrial wastes can therefore not be assumed without careful testing under realistic conditions.

Biological oxidation of ammonia consumes oxygen and, by definition in Standard Methods, is included as part of the BOD_5 test. However, much of the ammonia demand may not show up in five days because of inadequate seed bacteria or excessive competition from heterotrophic forms. The BOD_{20} is more realistic in assessing the oxygen demand due to ammonia in municipal effluents. The oxygen demand from ammonia in industrial effluents is best calculated assuming complete nitrification.

1) $2NH_3 + 4O_2 \longrightarrow 2HNO_3 + 2H_2O$

According to this equation, 1 mg of ammonia nitrogen could exert an ultimate BOD of 4.5 mg of oxygen. Well over 60% of the biological oxygen demand that will be exerted in receiving waters by biologically treated municipal effluents will be due to oxidation of ammonia to nitrate by the stream's flora. The BOD bottle is a relatively inefficient system for nitrification in comparison with the attached flora on the beds of the stream; therefore, reliance on the 5-day BOD bottle has shifted the burden of satisfying nitrogenous oxygen demand from the treatment plant to the receiving water.

It would be beneficial if waste treatment plants were required to produce nitrified effluent. Ammonia nitrogen in effluent has several undesirable features:

(1) Ammonia consumes dissolved oxygen in the receiving water;
(2) Ammonia reacts with chlorine to form chloramines which are less effective disinfectants than free chlorine;
(3) Ammonia is toxic to fish life;
(4) Ammonia is corrosive to copper fittings;
(5) Ammonia increases the chlorine demand at waterworks downstream.

A nitrified effluent, free of substantial concentrations of ammonia, offers several advantages:

(1) Nitrates will provide oxygen to sludge beds and prevent the formation of septic odors;

(2) Nitrified effluents are more effectively and efficiently disinfected by chlorine treatment;

(3) A nitrified effluent contains less soluble organic matter than the same effluent before nitrification.

In general, we can depend on conventional biological processes to transform almost all nitrogenous components in wastewater into ammonia and biological sludge. Once this has been accomplished, we can design systems to remove ammonia by air-stripping, or we can proceed to a second biological conversion of the ammonia into nitrates. A nitrified effluent may be acceptable for discharge, but if the nitrate level is too high it can be further treated by biological action to convert the nitrates to nitrogen gas.

Ammonia and nitrate are interchangeable nitrogenous nutrients for green plants and algae, as well as bacteria. Some species may prefer ammonia, and others nitrate, but in general they can be considered interchangeable (Flaigg and Reif, 1954). When algae grown on nitrates decompose they will liberate nitrogen in the form of ammonia.

Nitrogen and Eutrophication

The head of the National Eutrophical Program of the FWPCA has stated (Bartsch, 1970),

> "In many lakes that are in trouble because of eutrophication, the nutrients of prime significance are nitrogen and phosphorus. Phosphorus is found to be critical in terms of extensive production more frequently than nitrogen. In some cases it has been demonstrated through field study and appropriate assays that nitrogen does occupy a critical role. Reasons for pessimism relative to nitrogen control (of eutrophication) are the following:
>
> "(1) Many microorganisms can fix atmospheric nitrogen and make it available. Included are bacteria, some of the blue-green algae which are causes of bloom problems, and actinomycetes.

"(2) Nitrogen can pass through the soil and into the ground water and find its way into surface waters more easily than phosphorus. Ammonia can also find its way into surface water via precipitation, in some locations up to as much as 20 lbs/acre per year.

"Situations where nitrogen control must be used for control of eutrophication include the upper San Francisco Bay, where it has been demonstrated that nitrogen is the critical element. There is some thought that lakes that are young in the aging process are more likely to be nitrogen limiting than lakes that have started down the pathway of eutrophication. Lake Tahoe is an example where nitrogen may or may not be a limiting nutrient. In some bodies of water where phosphorus may be limiting part of the time during the growing season, nitrogen may normally be limiting at other times. It is possible to exercise some guided judgment in the matter of limiting nutrients through use of test procedures like the Provisional Algal Assay Procedure (PAAP, 1969)."

Nitrogenous Oxygen Demand

The Chief of the Engineering Section, Chesapeake Technical Support Laboratory, Middle Atlantic Region, FWQA, has stated in regard to nitrogen removal needs (Jaworski, 1970):

"In the upper Potomac Estuary about one half of the dissolved oxygen sag is due to a nitrogenous demand of organic matter being discharged from wastewater effluents in the Washington metropolitan area. During the low-flow summer months, dissolved oxygen levels of less than 2 mg/l in a 10-mile reach are common. Studies by CTSL, FWQA and Maryland Department of Water Resources have established that the dissolved oxygen deficits in the middle portion of the Patuxent River basin are mainly attributable to the nitrogenous demand of organic matter originating from wastewater discharges.

"To eliminate the dissolved oxygen deficit in the Potomac Estuary and in the Patuxent River, the removal of nitrogenous demand is required to manage the water quality in both areas. The State of Maryland has gone on record as requiring a maximum of 1 mg/l of ammonia in effluents discharging into the Patuxent River. To enhance the water quality of the Potomac River basin, the recent Potomac Enforcement Conference required 85% removal of the present nitrogenous oxygen demand from treated waste discharges in the Washington metropolitan area.

Algal Growth Response

"At the present time, predictive generalizations cannot be made for the response of algae to nutrients for all receiving waters. Different geophysical systems appear to be responsive to different limiting nutrients.

"In the Potomac Estuary during summer periods, nitrogen appears to be the rate limiting nutrient at the salinity-freshwater interface. Data from the James River Estuary by VIMS also indicate that the rate limiting nutrient is nitrogen. Thus it appears that nitrogen can be a manageable nutrient with respect to the control of eutrophication.

"If a wastewater system is selected that converts all or most of the nitrogen to nitrates, this will aid the immediate oxygen deficit caused by the oxidation of NH_3 to NO_3. Since NO_3 can be readily converted to organic nitrogen and NH_3 by bacteria and algal cells in waters, the potential nitrogenous demand will still be present. Therefore, carbon and phosphorus as well as nitrogen are the important parameters in the control of eutrophication with respect to the elimination of nuisance algal conditions and the enhancement of water quality.

"While the control of organic carbon and phosphorus will reduce the incidence of algal blooms, the addition of nitrogen removal will further enhance the control of the blooms. If wastewater treatment processes are added to convert the nitrogen to NO_3 without considering the complete removal of nitrogen, we are just transporting the problem farther downstream."

The State of Illinois has recently set an effluent standard of 2.5 mg/l of ammonia (2.05 mg/l ammonia-N) for discharge to surface waters. A substantial fraction of the oxygen sag in the Grand and Clinton Rivers in Michigan and in the Kanawha River, West Virginia, below a large industrial complex, has been attributed to the BOD of ammonia. It was early practice in Britain to nitrify effluents as evidence of good biological treatment since nitrification is difficult in the presence of large amounts of readily decomposable organic matter. Furthermore, nitrates in the water provide oxygen to help oxidize organic matter present from other sources, and to prevent septicity. Nitrates, usually as chili saltpeter, have frequently been used to control septic odors in estuaries and lagoons (Lang, 1966).

A review article of British water pollution control (Jenkins, 1970) states that a recent requirement limits ammonia nitrogen in sewage effluents not to exceed 10 mg/l. This means that a treatment plant must be designed to give complete purification to three times the dry weather sewage flow and that 60% to 70% of the ammonia nitrogen must be oxidized at all times. River control agencies regard nitrification as desirable because of the high oxygen demand of ammonia nitrogen, the toxicity of ammonia to fish under certain circumstances, the reduction in chlorine demand, and the oxygen reserve present in nitrates.

Ammonia is rapidly adsorbed by soil minerals and particulate matter containing nitrogen is also effectively removed in the soil. However, if there is not sufficient plant growth in the soil to use the bound ammonia, it will be converted to nitrates by nitrifying bacteria. Nitrates are very poorly adsorbed in the soil, and rapidly reach the ground water when present in excess. Therefore, over-fertilization with nitrogen compounds, whether they be ammonia, slow-release nitrogen, or nitrates, can lead to high concentrations of nitrates in ground water.

Ammonia has very little toxicity to humans and there are no limits on ammonia in the USPHS Drinking Water Standards of 1962, or the WHO International Standards. Ammonium compounds have been used in cooking and ammonia gas is the essential ingredient of smelling salts. Various suggested limits on ammonia in drinking water are related to the fact that ammonia is generally taken as an indicator of fecal pollution and the fact that high levels of ammonia dissolve copper from plumbing. The toxicity of ammonia to fish and other aquatic species is much higher than for humans, but details have not been completely elucidated. According to many references, the toxicity of ammonia and ammonium salts to aquatic animals is directly related to the amount of undissociated ammonium hydroxide in the solution, which in turn is a function of pH. Toxicity has been reported at levels as low as 0.2 mg/l of undissociated ammonia nitrogen (McKee and Wolf, 1963).

Nitrates have low toxicity for plants and animals. Saltpeter has traditionally been used as a curing agent for ham and is denitrified by bacteria in the intestines. However, some very young babies do not have a complete intestinal flora. The bacteria which are present reduce nitrates to nitrites, and do not carry the reduction further to nitrogen gas. Nitrites combine with hemoglobin to produce methemoglobinemia, a disease characterized by cyanosis. PHS and WHO standards recommend not more than 10 mg of nitrate nitrogen (45 mg nitrate) for water to be fed to babies. Many well waters contain more than 10 mg of nitrate nitrogen, and particularly among poorer classes and migrant laborers it is very difficult to make sure that babies are not given this water.

The following papers discuss specific processes which can be used to remove nitrogen compounds from water.

Paper No. 2

NITROGEN REMOVAL BY BIOLOGICAL SUSPENDED GROWTH REACTORS

E. F. Barth

Other sections of this report deal with chemical and physical processes to remove nitrogenous components of wastewater. While these are being actively investigated, our basic capability resides in carefully managed biological systems. Success in providing a high efficiency for nitrogen removal by biological denitrification requires that the biological transformation of ammonia nitrogen to nitrate nitrogen be under good process control. Any reduced nitrogen compounds introduced into the denitrification stage will pass through the process unaltered and impair overall nitrogen removal efficiency.

Downing and Hopwood (1964) revealed the complex factors involved in maintaining nitrification with a conventional activated sludge system. A three sludge variation of the activated sludge process has been developed which greatly simplifies the process control problems associated with maintaining nitrification (Barth, et al., 1968). Figure 1 is a schematic of the process developed for nitrogen removal by biological denitrification. Figure 2 is a representation of a municipal application of the three sludge system taking advantage of common wall construction techniques for economy in construction.

The three sludge system allows management of the separate biological transformations which are necessary for successful denitrification. As shown on Figure 1 the high rate system handles the bulk of the carbonaceous removal and at this station the waste activated sludge is removed. Thus, the nitrification stage receives a predominantly ammonia nitrogen feed and an enriched culture develops because each system has its own sludge recycle. This process design also has other desirable features. The high rate system protects subsequent nitrification stages from toxic chemicals. Heavy metals, cyanides, thiocyanates, and toxic organic chemicals will be either sorbed or biologically degraded before they reach the nitrification stage. Since this is a staged system there can be no direct short circuiting of materials from the influent to the effluent. Temperature effects on the enriched culture of the nitrification stage are not as extreme as

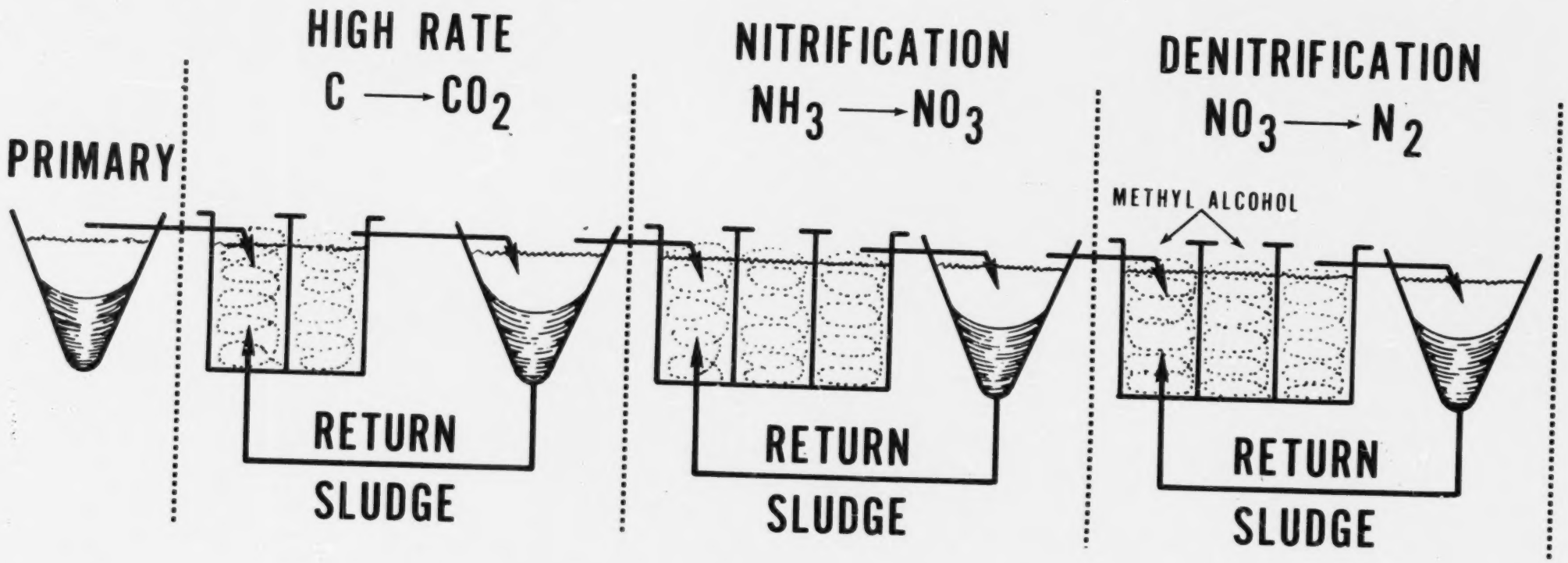

FIGURE I

THREE SLUDGE SYSTEM FOR NITROGEN REMOVAL

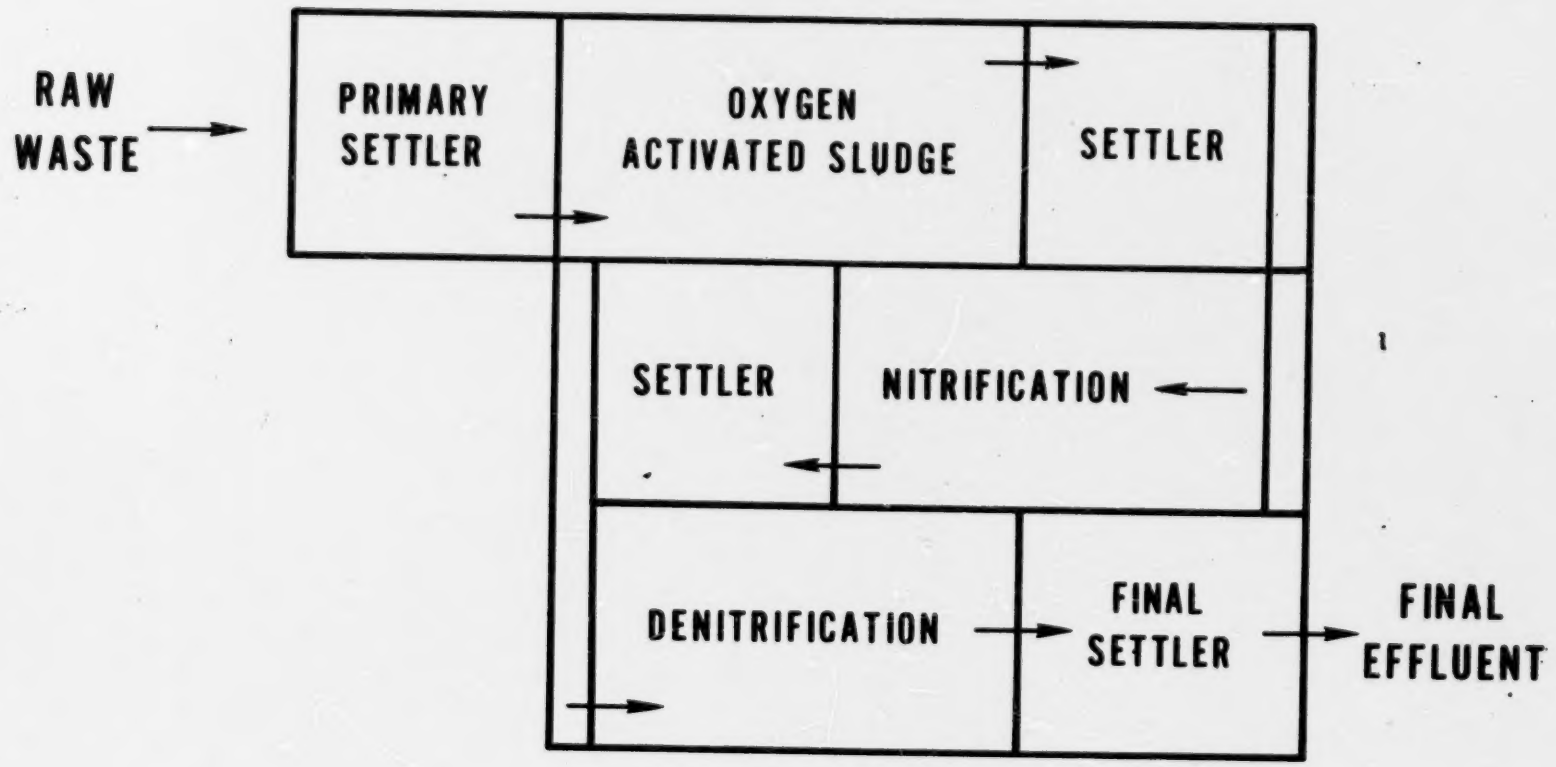

FIGURE 2

COMMON WALL CONSTRUCTION OF 3-SLUDGE SYSTEM

with a single sludge system which contains only a marginal population of nitrifying organisms.

Once controlled nitrification has been established the biological denitrification process can be optimized. The nitrified effluent flows to a stirred anaerobic reactor where methyl alcohol is added in proportion to the nitrate nitrogen concentration. The organisms in this stage use the oxygen component of the nitrate radical to oxidize the organic carbon of methyl alcohol. The end products of this metabolism are elemental inert nitrogen gas and carbon dioxide, which are liberated to the atmosphere.

The stage approach to nitrification has been investigated through grant and contract activities and work at the Robert A. Taft Water Research Laboratory. Large pilot plant operations are located at the University of Notre Dame and Manassas, Virginia. The process has also been evaluated at a 1 MGD scale at Hazel Crest, Illinois. Temperatures as low as 6° C have been recorded, with no detrimental effect on nitrification. Previous experience with the stage approach to nitrification has been reported by English and South African investigators (Osborn, 1965).

Biological denitrification has been studied by microbiologists for many years, particularly in regard to loss of nitrogen from soils (van Schreven, 1963). There have been intensive recent studies related to the application of denitrification to wastewaters. Wuhrman (1960) and Bringmann and Kuhn (1965) have both published in Europe. American experience includes studies at the Robert A. Taft Water Research Laboratory (Barth, et al., 1968); the Lebanon Plant, Firebaugh, California (McCarty, et al., 1969); Notre Dame, Indiana (Echelberger and Tenney, 1969); Manassas, Virginia (Mulbarger, et al., 1969); and Pomona, California (Carey, 1968). A summation of these studies show that biological denitrification is a controllable process if the reaction is forced with an organic supplement, such as methyl alcohol. Attempts to use waste organic matter from sewage have been less successful.

Packed column processes as well as suspended growth reactors have given efficient nitrogen removal. Large scale municipal application, in the range of 2 MGD or greater would favor suspended growth reactors. The 300 MGD Blue Plains Washington, D. C. municipal facility tentatively is

being designed on the basis of a three-stage biological system for both nitrogen and phosphorus removal after an extensive review of both chemical-physical approaches and biological approaches to nitrogen removal.

The Blue Plains plant will employ a final filtration step to assure quality control of the effluent. Filtration of effluents is necessary for high efficiency whether we are considering suspended solids, chemical oxygen demand, nitrogen, or phosphorus. We must have positive control of the solids no matter what treatment process we employ.

Figure 2 showing the municipal application of this process indicates that the current technology development of high purity oxygen for carbonaceous removal can be combined with this staged system to give very reasonable detention times. A two hour oxygen aeration period combined with one hour detention in each of the settlers, and two hours each for nitrification and denitrification give a total flow through time of ten hours.

The three-stage biological system can produce an effluent containing 2 mg/l, or less, of total nitrogen. This is a very realistic figure to use as an effluent standard, and when dealing with municipal wastewaters it represents 90 percent or greater removal of total nitrogenous materials.

The capital cost of such a system would be about 25 percent more than a conventionally designed activated sludge process of equal flow. The use of high purity oxygen in the first and second stages could bring the capital cost almost exactly in line with conventional capital costs.

The operating cost for the methyl alcohol to supplement the denitrification process is 3 cents per thousand gallons for a wastewater containing 20 mg/l of nitrogenous material.

Paper No. 3

NITROGEN REMOVAL FROM WASTEWATERS BY COLUMN REACTORS

J. M. Smith

Once nitrates are formed in sewage treatment they can be converted back to nitrogen by the action of microbes and a source of BOD. Columnar nitrate reduction represents a second alternate to the suspended growth systems as a means of biochemically reducing the nitrate ion to elemental nitrogen (see Figure 3). A variety of facultative bacteria common in wastewater including the genera Pseudomonas, Achromobacter and Bacillus are known denitrifiers. When supplied with a suitable organic carbon source under anaerobic or near anaerobic conditions these organisms use nitrates and nitrites as the terminal hydrogen acceptors during the fermentation of the added substrate to ultimately form nitrogen gas.

In a packed column the cell residence time of the surface bound slime is much greater than the hydraulic detention time. This, combined with a large contact surface and short diffusion distances afforded by small media such as sand, provides an efficient system for rapid denitrification of an applied feed.

Work at Lebanon, Ohio (J. M. Smith, 1970, Unpublished) has shown that the smaller media systems (sand to 3/4 inch diameter stone) are effective when operated downflow at surface loading rates of 7.0 gpm/ft and at actual contact times of 5 to 30 minutes. The downflow operation, using either granular carbon or sand, requires daily backwashing using 1-3 percent of the throughput stream to relieve pressure drop due to the accumulation of suspended solids in the upper portion of the column. The denitrifying slime is firmly attached to the media surface, and is not removed during the backwash operation. Greater than 90 percent nitrate reduction can be achieved within these columns at contact times of 10 minutes for sand and 30 minutes for the 3/4 inch stone. The effluent normally contains less than 2.0 mg/l of nitrate nitrogen with effluent turbidities less than 3 JTU, indicating little solids contribution from the attached organisms. The ammonia and organic nitrogen content of the feed is not significantly changed during the denitrification process.

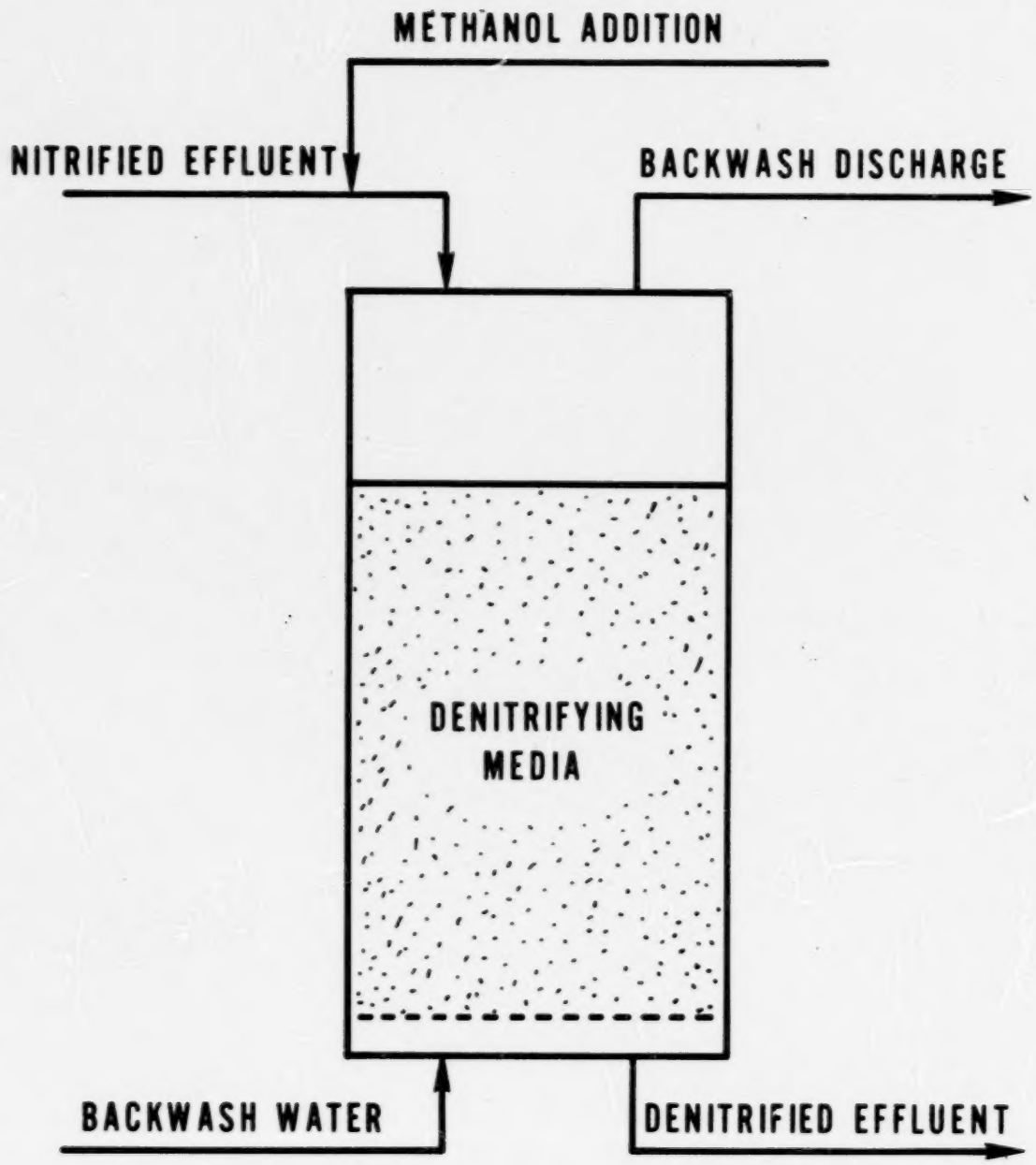

FIGURE 3

PACKED BED DENITRIFICATION REACTOR

Larger media varying in size from 1 inch to 2 inch aggregate has been successfully employed to denitrify agriculture subsurface drainage (Tamblyn and Sword, 1969). The larger media permits upflow operation without backwashing at the expense of longer contact times and increased effluent suspended solids. Nitrate reduction of greater than 90 percent can be achieved in contact times of 1 hour for the 1 inch aggregate and 2 hours for the 2 inch aggregate at temperatures above 12° C. The 2 inch columns have been operated continuously for over six months on agriculture subsurface drainage without the loss of efficiency or solids accumulation.

Methanol is used as the supplemental organic carbon source of choice for denitrification because of its low cost, biodegradability and ease of handling. Approximately 3 mg of methanol are required per mg of NO_3-N removed including the requirement for deoxygenating the nitrified feed. The chemical cost for removing 20 mg/l of NO_3-N in the presence of 5 mg/l of dissolved oxygen is estimated to be 1.6¢/1000 gal.

While the packed bed provides an efficient contacting system for denitrification, total nitrogen removal via biological nitrification-denitrification will depend on the combined efficiency of the nitrification stage as well as the denitrification stage. This interdependence of two biological systems will limit total nitrogen removal efficiencies to a practical value of about 90 percent.

Pilot plant experiences to date firmly support a full scale demonstration of columnar nitrate reduction at the 1 MGD level or above. One possibility is the construction of a new facility that incorporates a two stage nitrifying system followed by columnar denitrification. An alternate, and equally plausible idea is to modify an existing conventional activated sludge process by splitting the aeration tanks into a two sludge system by the addition of a second settler, perhaps a tube settler, followed by denitrification on a relatively fine media that will also serve as a solids polishing process. The design of a denitrification system is straightforward and involves basic principles of biological oxidation and filtration. When furnished with basic denitrification data any competent sanitary engineering firm should be able to successfully design a treatment plant capable of removing nitrogen.

Paper No. 4

AMMONIA NITROGEN REMOVAL BY STRIPPING WITH AIR

J. B. Farrell

Ammonia is a gas which dissolves in water to an extent controlled by the partial pressure of the ammonia above the water. An increase in its partial pressure causes more ammonia to dissolve, reducing its partial pressure causes ammonia to leave the water phase and enter the gas phase. If it is desired to remove ammonia from water, this can be done by contacting the water with a sufficient quantity of ammonia-free air. This physical process is called desorption or, more commonly, "stripping."

Wastewater contains the ammonium ion at concentrations which typically range from 15 to 25 mg/l. If the ammonium ion is converted to dissolved ammonia by raising the pH, the ammonia may be stripped out by contacting the wastewater with air. Early studies of feasibility of stripping of ammonia from wastewater (Kuhn, 1956) showed a major difficulty: the volume of air per unit volume of water is very high, about 400 cubic feet per gallon of water in a countercurrent-flow packed tower. The pressure drop across a packed tower is about 1.0 psi or 28" of water. Since power is proportional to the product of volumetric flow rate and pressure drop, the cost for power made the process prohibitive even at this relatively low pressure drop.

The problem of high power cost was solved by investigators at the South Lake Tahoe Public Utility District (Slechta and Culp, 1967) who used a slat-filled tower such as is used for cooling water to contact water and air. The pressure drop across such a device is very low--about 1/2 inch of water--so power costs are reduced to reasonable levels. Removal efficiencies as high as 90 percent were obtained in a 24-foot high tower in which water and gas were contacted in a nearly countercurrent fashion. On the basis of this experience, a full scale stripping tower was constructed at South Lake Tahoe. The tower was designed to remove 90 percent of the ammonia from 3-1/2 MGD of Tahoe's renovated wastewater. The air flow is not countercurrent to the water but flows across the tower (cross-flow), while the water drips downward through the packing.

Initial operation of Tahoe's stripping tower was in the winter and immediately revealed a limitation of ammonia stripping. The cold air contacting the wastewater quickly cooled the water. Ammonia solubility is higher in cold water than in warmer water; consequently, more air is required to remove it. For example, at 0° C it would take about 800 cubic feet of air per gallon of water to remove 90 percent of the ammonia from wastewater in a countercurrent tower. Since the Tahoe tower was designed for 400 cubic feet per gallon, percent removal was much lower than 90 percent. When air temperature fell below 0°, freezing of water occurred at the air inlets, making the tower inoperable. From theoretical considerations, difficulty with freezing may be anticipated when the wet-bulb temperature of the ambient air is below 0° C.

Another problem which developed at Tahoe is the formation of scale in the tower. The scale is chiefly calcium carbonate. It forms because the previously lime-treated effluent is supersaturated with respect to calcium carbonate. A more important reason is the presence of carbon dioxide in the air. A small portion of the carbon dioxide reacts with the basic wastewater, forming calcium carbonate which precipitates. In the case of the tower at Tahoe, the sludge can be flushed from the tower except from inaccessible areas which cannot be reached with a water jet. A pilot plant ammonia stripping tower at Blue Plains, Washington, D.C., has had similar scaling problems, except the scale is hard and adheres to the tower fill. A pilot tower in New England had similar hard scale (Sawyer, 1970). However, a pilot plant tower has been run in South Africa (van Vuuren, 1970), and here the scale has been so soft that the force of the water dripping through the tower fill has been sufficient to flush out the scale.

The causes of the differences in the nature and amount of scale in various locations has not been resolved. Some suggested factors influencing the nature of the scale are: type of contact (countercurrent or cross-flow), recirculation of sludge, pH of the wastewater, and chemical makeup of the wastewater. Studies are in progress to see if the scale can be prevented from forming, or if it can be made nonadherent.

The cost of ammonia stripping has been estimated by Suhr (1969) for South Lake Tahoe facility to be about 2.9¢ per 1000 gallons of wastewater treated. This does not include the cost of the lime and facilities to raise the pH to about 11. These costs have been charged to phosphorus removal because this is the direct objective of the lime addition. If 90% removal of ammonia nitrogen is required even in cold weather, these costs should be increased by about 50% to provide for a higher air-to-water ratio. In below-freezing weather the tower will be inoperable. It is possible to heat the incoming air to temperatures above 0° C and add moisture to it to prevent freezing. This procedure would only be economical if subfreezing days are rarely encountered.

Methods for designing ammonia stripping towers have been developed at the Taft Center by Roesler et al. (1970) but have not yet appeared in the literature. Ammonia stripping is feasible when the temperature is above freezing but there is danger of serious fouling by scale. The best approach for minimizing scale and its effects appears to be to use a pH of about 10.5, countercurrent operation rather than cross-flow, and an open fill to allow for easy flushing of accumulated solids.

Paper No. 5

REMOVAL OF AMMONIA NITROGEN BY SELECTIVE ION EXCHANGE

R. B. Dean

Ammonia exists in solution predominantly as the ammonium cation (NH_4^+) unless the pH is higher than about 9.5. The ammonium ion is very similar to the potassium ion in size and is precipitated by the same reagents that precipitate potassium. Adsorption of ammonium ion on ion exchange resins is ordinarily very similar to the adsorption of potassium or sodium ions. Therefore, conventional water softening ion exchange resins which are selective for calcium and magnesium do a relatively poor job of removing ammonium from dilute solutions. Total deionization by mixed bed ion exchange resins will, of course, remove ammonium ions along with other cations but this process is too costly for wastewater treatment.

Certain zeolites show unusual selectivity for the ammonium ion. A number of these have been investigated by the Atomic Energy Commission because they also show selectivity for cesium and potassium ions. A demonstration project at the Battelle Memorial Institute - Pacific Northwest (Hanford) Laboratories, 1969 (see Mercer, 1970), showed that certain zeolites, including the naturally occuring mineral clinoptilolite, had a high selectivity for ammonium in natural and wastewaters. A trailer mounted demonstration plant with a capacity of 100,000 gallons per day was built as a cooperative demonstration project between the FWQA and Battelle-Northwest. This trailer is now operated under contract to the FWQA to demonstrate selective ion exchange removal of ammonium ions from solution.

Preliminary work demonstrated that native clinoptilolite from Hector, California, could be used after grinding and sieving to 20 x 50 mesh. When columns filled with this material were fed secondary effluent they clogged rapidly; therefore, the trailer incorporates an inclined-tube settler clarifier to remove turbidity from the feed. Clarified water is treated by conventional downflow through two columns in series. When ammonia breaks through the second column, the first column is taken offstream and a third column containing freshly regenerated clinoptilolite is added after the second column which now becomes the first in the series. The loaded column is regenerated by backwashing with limewater containing sodium chloride to

speed up the rate of regeneration. The concentration of sodium chloride is approximately that which will be reached after several regeneration cycles. The high pH of the limewater converts the ammonium ion to unionized ammonia gas in solution. This is allowed to build up to a level of about 500 mg/l by recycling of the limewater. Precipitates such as magnesium hydroxide which may form in some hard waters are removed by settling.

The ammonia laden limewater is then pumped through a packed column through which heated air is blown to remove the ammonia. The problems of ammonia dispersal to the atmosphere are similar to those encountered in direct air stripping of ammonia. However, the ammonia content of the gas stream is 20 to 50 times as strong as occurs with direct air stripping and there is proportionately much less air to be heated in cold weather. On a large scale it would probably be more economical to use stripping towers of the cooling tower type rather than packed towers because the latter have very high pressure drops. However, a packed tower is much more compact and could be incorporated in the available space on the trailer.

Because of the high concentration of ammonia, its odor is readily detectable in the effluent gases. Of course, the total amount of ammonia vented to the atmosphere is the same whether ammonia is stripped directly or is first concentrated in an ion exchange column. Direct stripping of ammonia from municipal effluents would produce a concentration of ammonia nitrogen in the air of approximately 0.03 ppm, which is well below the threshold for detection by odor.

Ammonia in the atmosphere reacts with sulfur dioxide which is present in large excess over all cities. If all of the ammonia present in sewage in the United States were to be discharged to the atmosphere, it would be equivalent to less than 10 percent of the sulfur dioxide being discharged to the atmosphere. Ammonia and SO_2 together can cause fog under some conditions; however, unneutralized sulfur dioxide eventually forms sulfuric acid which is even more objectionable. Further studies on the behavior of ammonia in urban atmospheres are warranted.

Ammonia gas in the atmosphere, whether or not it reacts with sulfur oxides, is adsorbed by moisture in soil, vegetation, and open water

surfaces. That portion which goes into the soil and vegetation will be bound and will no longer be a pollutant. However, if prevailing winds would blow ammonia laden air over inland bodies of water, as for example at Toledo, then ammonia stripping to protect surface waters would not be appropriate.

The cost of removing ammonia by ion exchange has been estimated by Eliassen as 8.1¢/1000 gallons. His estimate includes the cost of brine for regeneration but does not include the cost of disposal of the ammonia laden brine. In most areas this could be a serious problem since discharge to surface waters would be self-defeating. Pilot studies at Battelle-Northwest indicated a cost of between 3 and 6¢/1000 gallons for their Zeolite method. In view of difficulties found in the field, it is likely that the upper level will be a safe estimate. More reliable cost estimates will be available at the conclusion of the present contract with Battelle-Northwest. Alternative methods of regenerating zeolites which convert the ammonia to nitrogen gas are also being investigated.

Paper No. 6

ION EXCHANGE FOR NITRATE REMOVAL

R. A. Dobbs

Ion exchange is a standard unit process in the water treatment field. Large units have been installed for softening municipal water supplies. The resins used are fairly selective for the divalent cations of calcium and magnesium which are responsible for most of the hardness in water. Unfortunately, a comparable resin with a high selectivity for nitrate ion over other anions does not exist.

A technical and economic evaluation of the feasibility of removing nitrate from irrigation return drain water has been made by the Dow Chemical Company (1968). Although the concentration of anions in the drain water is considerably higher than the corresponding concentration in wastewater, the ratio of nitrate to chloride is quite similar for both waters. Several conclusions related to the drain water can be extrapolated to municipal wastewater. Commercially available anion exchange resins have a selectivity for nitrate over chloride. In order to develop an economic process this selectivity ratio should be approximately 20.

Even if resins of the required selectivity could be developed, additional problems must be solved in order to make the process practical. Regeneration of selective ion exchange resins are usually difficult. Based on the nitrate anion alone, efficiency of sodium chloride regeneration is of the order of 1%. Another serious problem involves the ultimate disposal of the nitrate laden brine produced during regeneration. Theoretically, resin regeneration could be achieved with sodium sulfate. Nitrate could be reduced chemically with ferrous sulfate and neutralized with lime to produce sludges and nitrogen gas as discussed in the next section. However, chemical and sludge disposal costs are likely to make the process uneconomical. In the brine regeneration process the high concentration (15%) of salt suggests the possibility of electrochemical treatment of the regenerant to produce nitrogen gas and chlorine.

Several attempts have been made to develop selective ion-exchange processes for nitrate removal. Dow Chemical Company is presently under contract (Contract No. 14-12-808) to develop a nitrate removal process based on the use of a porous solid absorbent containing a nitrate-selective

water-immiscible extractant. The process has the advantages of liquid ion-exchange technology and the ease of operation of the granular bead resin systems.

Selective nitrate removal by ion exchange will not be feasible until new resins are synthesized with a high selectivity for nitrate over other anions present in the water. In addition, a suitable process for treating the nitrate laden regenerants must be developed.

Paper No. 7

OTHER METHODS FOR REMOVING NITROGEN

R. B. Dean

In addition to ammonia, nitrites and nitrates already discussed, nitrogen can occur in wastewaters in several other forms. Small concentrations of amino acids are leached from bacteria under anaerobic conditions. Digester supernatants contain a relatively high concentration of soluble amino acids and secondary clarifiers may release substantial quantities of amino acids if anaerobic conditions are approached in the return sludge. Amino acids are readily biodegraded and are removed in part by lime precipitation and carbon columns. Nitrilotriacetic acid (NTA) has been proposed as a detergent additive to chelate calcium ions as a partial replacement for phosphates. NTA is biodegraded in a well-operated secondary treatment plant. (Bunch and Ettinger, 1967) It is not removed by precipitation with aluminum hydroxide. The behavior of NTA toward precipitation by lime or iron salts and its behavior in the column of activated carbon containing adsorbed organic matter and a bacterial flora are now being studied at Cincinnati. NTA levels in wastewater are not expected to exceed about 2 mg/l as nitrogen.

Urea is the principal form in which nitrogen is excreted. Fortunately, urea is rapidly hydrolyzed to ammonia by bacteria in sewer lines and biological treatment plants. In the absence of biological action it would be extremely difficult to precipitate or adsorb urea from solution. Organic nitrogen is also present in particulate form both in raw sewage and in secondary effluents. In the latter case bacteria and bacterial fragments account for nearly all the suspended nitrogen. Efficient clarification and filtration are effective ways of removing this form of nitrogen. Typically, the organic nitrogen in the product from a carbon column following secondary treatment is approximately 1.0 mg N/l. This residue has not been characterized but it may be derived from bacterial action.

Soluble nitrogen compounds, with the exception of urea, are all ionized in water and 85-90 percent of them can be removed by any deionizing or desalting process such as reverse osmosis, electrodialysis, ion exchange or distillation. None of these processes have a favorable selectivity for ammonium or nitrate ions and it is, therefore, necessary to remove about

90 percent of the salts in order to remove 90 percent of the soluble nitrogen compounds. Distillation is particularly unfavorable since it tends to concentrate ammonia in the distillate unless the feed is kept highly acidic. In that case, nitrous acid will be selectively distilled over. (O'Connor et al., 1967) All of the general salt removal techniques are of interest only for water that is to be reused and are too expensive for consideration as treatments for wastes to be dischared to surface waters.

Chlorination of Ammonia. Ammonia reacts with chlorine to the breakpoint according to the theoretical breakpoint equation.

$$(1)\quad 3Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCL$$

Actually $4Cl_2$ is required and this means that higher oxides of nitrogen be produced. A large number of possible compounds may be formed but unfortunately it is difficult to identify them analytically without very sophisticated procedures. Four moles of chlorine per mole of N_2 corresponds to 10 parts of chlorine for each part of ammonia nitrogen. The per capita excretion of ammonia nitrogen is of the order of 10 lbs. per year, equivalent to 100 lbs. of chlorine. A city of 200,000 would, therefore, require about 20 million lbs. or 10,000 tons of chlorine each year. Transport and handling of this amount of chlorine would be hazardous. Also, the use of chlorine would produce an equivalent weight of hydrochloric acid, which would exceed the buffer capacity of most waste waters, and would produce the highly odorous NCl_3. While hydrochloric acid would be effectively neutralized by discharge into the ocean and most surface waters, it could be a serious pollutant and discharge pipes would have to be made of special acid resistant materials. Sodium or calcium hypochlorite can be substituted for chlorine of equation (1).

$$(2)\quad 3NaOCl + 2NH_3 \longrightarrow N_2 + NaCl + 3H_2O$$

No excess hydrochloric acid is produced by the use of sodium hypochlorite, but again it will be necessary to use four moles of hypochlorite per mole of nitrogen or equivalent. Hypochlorite is more expensive than chlorine but is so much safer to use that New York City, Chicago, and other large cities have converted to aqueous hypochlorite for chlorination of water and treated wastes.

Chlorine is manufactured electrolytically according to equation (3):

(3) $2NaCl + H_2O \longrightarrow H_2 + Cl_2 + 2NaOH$

Sodium hypochlorite is made by the reaction of chlorine and NaOH. If this is done in the electrolytic cell, equation (4) results.

(4) $NaCl + H_2O \longrightarrow H_2 + NaOCl$

Electrochemical production of chlorine or sodium hypochlorite has been practiced for sewage chlorination and treatment for years (Marson, 1967). It has never been optimized. Some source of brine is necessary to raise the conductivity of the water; therefore, electrochemical production of chlorine or hypochlorite has only been attractive for seacoast communities. Breakpoint chlorine treatment, of course, also disinfects as well as destroys ammonia. However, the addition of 200-300 mg/l of chloride might not be acceptable in inland waters.

Just as ammonia can be oxidized to nitrogen, so can nitrate be reduced to nitrogen. In acid media, nitrous acid derived from nitrites reacts with ammonia and amines to liberate nitrogen gas.

(5) $HNO_2 + RNH_2 \longrightarrow ROH + N_2 + H_2O$

This reaction, called the Van Slyke reaction, does not proceed in neutral waters. (Brezonik and Lee, 1966) Chemical reduction of nitrates in dilute solution has been accomplished using ferrous sulfate to produce nitrogen gas and some nitrous oxide, N_2O. (Gunderloy et al., 1968) The by-product is a voluminous sludge of ferrous-ferric hydroxide. Some of the sulfate is incorporated in the precipitate but a large part of the sulfate remains in the waste. This process is being studied under contract and at present appears to have marginal value for special situations.

Costs of any of the processes discussed in this section are probably higher than costs for the more promising processes. The only cost that can be calculated direct with some confidence is the cost for chlorine to oxidize ammonia. Assuming 20 parts of ammonia nitrogen in a secondary effluent, 200 parts of chlorine would be required for breakpoint chlorination. This is equivalent to 1.5 lbs. of chlorine per 1000 gallons or about 6¢/1000 gal. To this must be added the cost of handling the corrosive hydrochloric acid produced. Sodium hypochlorite may cost twice as much as chlorine but associated costs are greatly reduced. The cost of electrically generated chlorine or hypochlorite will depend on the cost of electrodes and the possibility of using low-cost off-peak power.

BIBLIOGRAPHY

AWWA Committee Report, 1970. "Chemistry of Nitrogen and Phosphorus in Water," 62(2), 127-140.

Barth, E. F., et al., 1968. "Chemical-Biological Control of Nitrogen and Phosphorus in Wastewater Effluent," J. Water Pol. Control Fed., Vol. 40, 2040.

Bartsch, A. F., 1970. Personal communication.

Battelle Memorial Institute, Pacific Northwest Laboratories, March 1969. "Ammonia Removal from Agricultural Runoff and Secondary Effluents by Selected Ion Exchange," U.S. Dept. of Interior, FWPCA, Report TWRC-5.

Brezonik, P. T., and Lee, G. F., 1966. "Sources of Elemental Nitrogen in Fermentation Gases," Air & Wat. Pol. Int. J., Pergamon Press, 10, 145-160.

Bringmann, G., and Kuhn, R., 1965. "Schnell-denitrifikation im underdruck-verfahren," Gesundheits-Ingenieur, Vol. 86, 16.

Bunch, R. L., and Ettinger, M. B., 1967. "Biodegradability of Potential Organic Substitutes for Phosphates," 22nd Annual Purdue Industrial Waste Conference, Purdue University, Lafayette, Ind., 393-396.

Carey, C., Sept. 1968. "Column Denitrification at Pomona, California," 41st Annual Conference Water Pollution Control Federation, Chicago, Illinois.

Dow Chemical Company, August 26, 1968. "Feasibility of Removal of Nitrates from San Luis Drain Waters by Ion Exchange," Final Report Contract No. 14-06-D-6434, U.S. Bureau of Reclamation, Department of Interior.

Downing, A. L., and Hopwood, A. P., 1964. "Some Observations on the Kinetics of Nitrifying Activated-Sludge Plants," Schweizerische Zeitschrift fur Hydrologie, Vol. XXVI, Fasc. 2, 271-288.

Echelberger, W. F., and Tenney, M. W., 1969. "Control of Organic and Eutrophying Pollutants by Combined Chemical and Biological Wastewater Treatment," Division of Water, Air and Waste Chemistry, American Chemical Society, Minneapolis, Minnesota.

Flaigg, N. G., and Reid, G. W., 1954. "Effects of Nitrogenous Compounds on Stream Conditions," Sewage Ind. Wastes, 26(9), 1145-54.

Gunderloy, F. C. Jr., et al., Oct. 1968. "Dilute Solution Reactions of the Nitrate Ion as Applied to Water Reclamation," U.S. Dept. of Interior, FWPCA, Report TWRC-1.

Jaworski, N., 1970. Personal communication.

Jenkins, S. H., 1970. "British Water Pollution Control," Environmental Science & Technology, 4(3), 204-209.

Kuhn, P. A., 1956. "Removal of Ammonium Nitrogen from Sewage Effluent," M.S. Thesis, University of Wisconsin.

Lang, M., 1966. "Chemical Control of Water Quality in a Tidal Basin," J. Water Pol. Control Fed., 38(9) 1410-18.

Marson, H. W., 1967. "Electrolytic Methods in Modern Sewage Treatment," Effl. Wat Treat. J., 7, 71-73 and 75-77.

McCarty, P. L., Beck, L., and St. Amant, P., May 6, 1969. "Biological Denitrification of Wastewaters by Addition of Organic Materials," 24th Annual Purdue Industrial Waste Conference, Purdue University, Lafayette, Indiana.

McKee, J. E., and Wolf, H. W., 1963. "Water Quality Criteria," 2nd Ed. Publication 3A, California State Water Quality Control Board, Sacramento, Calif., 134.

Mercer, B. W., Ames, L. L. Jr., Touhill, C. J., Van Slyke, W. J., and Dean, R. B., 1970. "Ammonia Removal from Secondary Effluents by Selective Ion Exchange," J. Water Pol. Control Fed., 42, R 95-107.

Mulbarger, M. C., et al., April 1969. "Manassas, Va., Adds Nutrient Removal to Waste Treatment," Water and Wastes Engineering, 46.

O'Connor, B., et al., 1967. "Laboratory Distillation of Municipal Waste Effluents," J. Water Pol. Control Fed., 39(10 part 2), R 25-31.

Osborn, D. W., 1965. "Operating Experiences with Double Filtration in Johannesburg," J. of the Institute of Sewage Purification, Part 3, 272.

PAAP, Feb. 1969. "Provisional Algal Assay Procedure," Joint Industry, Government Task Force on Eutrophication, P.O. Box 3011, Grand Central Station, New York, N.Y., 10017.

Roesler, J. F., Smith, R., and Eilers, R. G., 1970. "Mathematical Similation of Ammonia Stripping Towers for Wastewater Treatment," Internal Report, Advanced Waste Treatment Research Laboratory, Cincinnati, Ohio.

Sawyer, C., February 18, 1970. Personal communication.

Slechta, A. F., and Culp, G. L., 1967. "Water Reclamation Studies at the South Tahoe Public Utility District," J. Wat. Poll. Control Fed., 39(5), 787-813.

Smith, John M., May 1969 to March 1970. Data from experimental results contained in monthly report. Research concluded at Lebanon, Ohio, pilot plant by John M. Smith.

Stojanovic, B. J., and Alexander, M., 1958. "Effect of Inorganic Nitrogen on Nitrification," Soil Science 86(6), 208-215.

Suhr, L. G., 1969. "Nutrient Removal at Lake Tahoe, Costs and Criteria," communicated to R. B. Dean.

Tamblyn, T. A., and Sword, B. R., 1969. "The Aerobic Filter for the Denitrification of Agricultural Subsurface Drainage," 24th Purdue Industrial Waste Conference.

van Schreven, D. A., 1963. "Nitrogen Transformations in the Former Subaqueous Soils of Polders Recently Reclaimed from Lake Ijssel. Losses of Nitrogen Due to Denitrification and Leaching." International J. of Plant Nutrition, Plant Chemistry, Soil Microbiology and Soil-borne Plant Diseases, Vol. 17, 163.

van Vuuren, L. R., January 21, 1970. Personal communication to R. Culp.

Wuhrman, K., 1960. "Effect of Oxygen Tension on Biochemical Reactions in Biological Treatment Plants," Paper No. 3, Conference on Biological Waste Treatment, Manhattan College, New York.